

THEORY OF NITRATION OF SATURATED HYDROCARBONS AND THEIR  
DERIVATIVES: II. MECHANISM OF THE FORMATION OF GEM-DINITRO  
DERIVATIVES

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**CONFIDENTIAL**THEORY OF THE NITRATION OF SATURATEDHYDROCARBONS AND THEIR DERIVATIVES

## II. MECHANISM OF THE FORMATION

## OF GEM-DINITRO DERIVATIVES

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To determine the individual chemical effect of the monomeric form of nitrogen peroxide on alkylbenzene, we conducted an experiment in 1934 on the interaction of nitrogen peroxide with toluene [methylbenzene], the latter being highly diluted. Surprisingly, the primary product in this case proved to be phenyldinitromethane  $C_6H_5CH(NO_2)_2$ , *for the first time* initially separated by nitration of toluene. A systematic analysis of this reaction disclosed the highly paradoxical dependence of the *yield ratio* of phenylnitromethane and phenyldinitromethane on the conditions of the interaction. It was found that an increase in the concentration of nitrogen peroxide and a higher temperature caused, unexpectedly, a marked reduction in the yield of the dinitro-substitute and an increase in the formation of phenylnitromethane:

Molecular weight	$\frac{N_2O_4}{N_2O_4 + C_6H_5CH_3}$	0.04	0.15	0.46
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(1)

Ratio of yields in (g-mol)	$\frac{C_6H_5CH(NO_2)_2}{C_6H_5CH_2NO_2}$	3.7	1.4	0.9
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Temperature of reaction	--	20°	40°	70°	95°
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Ratio of yields in (g-mol)	$\frac{C_6H_5CH(NO_2)_2}{C_6H_5CH_2NO_2}$	3.6	2.2	0.32	0.08
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(2)

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In nitration, ~~as~~ <sup>the opposite</sup> as in all other reactions of similar type, ~~com-~~  
~~pletely~~ contradictory relationships have always been observed, ~~hitherto~~.

To our surprise, the experiment showed that phenylnitromethane was not an intermediate product in the formation of <sup>in</sup> ~~(?)~~-dinitrotoluene. In spite of established opinion ~~that hydrogen~~ <sup>(insert from following page)</sup> ~~possesses great chemical mobility when with carbon linked to a nitro-~~ <sup>attached to a</sup> ~~group, phenylnitromethane showed almost no change under the action of~~ <sup>which is</sup> ~~nitrogen peroxide or nitric acid under conditions corresponding to ni-~~ <sup>tration, or under even more rigid circumstances.</sup> ~~Only to a very slight extent did it change to benzoic acid [benzenecarboxylic acid].~~ <sup>was it converted</sup> ~~This, it~~ <sup>seemed, eliminated the most natural hypothesis with regard to the formation of phenyldinitromethane through mononitrocompounds.</sup> ~~seemed, eliminated the most natural hypothesis with regard to the formation of phenyldinitromethane through mononitrocompounds.~~

All these phenomena, which are in complete ~~contradiction to established~~ <sup>disagreement with</sup> ~~chemical opinion~~, are logically explained from the viewpoint of our theory ~~of~~ <sup>conventional chemical concepts,</sup> on nitration of saturated hydrocarbons; certain conclusions which, at first glance, ~~seem strange~~ <sup>confirmed</sup>, are fully justified by experiment. In this paper we will present the detailed theoretical basis for the previously ~~discussed formation process of this reaction (1)~~ <sup>advanced mechanism</sup> and will furnish fundamental experimental proof of it.

In accordance with our theory ~~(2)~~, the primary chemical action in the nitration of paraffins and the side chain of alkylbenzenes is the elementary process



leading to the formation of <sup>a</sup> free alkyl.

Let us examine the likelihood of conversion of ~~(1-word illegible)~~ <sup>formed</sup> radicals under conditions of nitration. Experiment and theory prove conclusively that the ~~speed with which radicals combine~~ <sup>rate of combination of</sup> among themselves, or with other molecules containing uncoupled electrons, is many  $(10^5$  and more) times greater than their interaction with saturated particles.

In the field of nitration, such radical-like molecules are nitric oxide and the monomer of nitrogen <sup>dioxide</sup> peroxide; their electronic structure

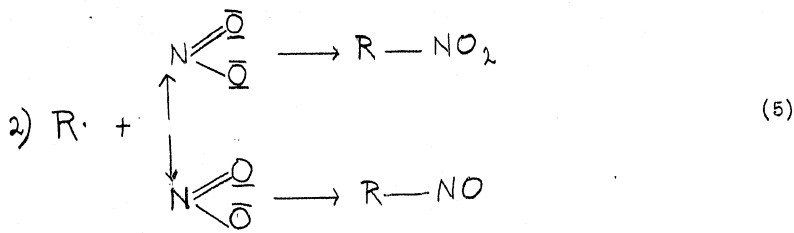
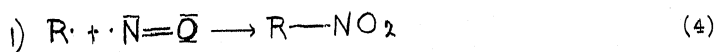
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(Note: The incorrectness of this opinion will be subsequently proven by us and the reasons for its arising explained -

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and reaction with the alkyls can be expressed as follows:



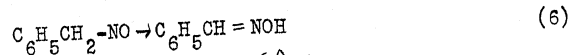
The reaction of alkyls with nitric oxide and nitrogen peroxide should also <sup>be taken into</sup> favor a marked difference in the character of <sup>the reagents</sup> their affinity to the electron <sup>are</sup> (the alkyls <sup>ie</sup> toward the nucleophiles, and the nitrogen oxides <sup>ie</sup> toward the electrophiles. The <sup>rate</sup> speed of ~~the~~ interaction between alkyls and other more or less <sup>saturated</sup> molecule-saturated systems will depend on the participation of radical forms in their structure, and electrostatic factors; a somewhat analogous case was discussed in the first report on the study of the interaction of NO<sub>2</sub> with hydrocarbons and their derivatives.

The rapid reaction of radicals with nitric oxide and nitrogen <sup>dioxide</sup> peroxide is confirmed by the results of experiments conducted by Schlenk and Wittig [3, 4] in their study of the action of these nitrogen oxides on triphenylmethyl and diphenylcyanomethyl. In recent years, considerable material has been compiled in the field of research on the photolytic and pyrolytic reactions of organic substances, proving <sup>undisputably</sup> ~~the~~ the high rate of reaction of the common alkyls (CH<sub>3</sub> etc) with nitrogen oxides. The method of "intercepting" emerging radicals, <sup>with nitric oxide</sup> first introduced by Hinshelwood in 1934, has gained wide application in proving their formation, as well as demonstrating the chain characteristics of the reaction; for example, we have recently discovered that the introduction of nitric oxide and nitrogen <sup>dioxide</sup> peroxide in the photochemical chlorination of n-pentane and cyclohexane [4] <sup>strongly brakes</sup> ~~considerably~~ <sup>is induced by irradiation</sup> ~~stimulated by~~ the process and interrupts the reaction, which ~~was~~ <sup>is</sup> stimulated by

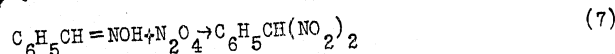
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The dimensions of exposure. This line of thought in our theory on the interaction of nitric oxide and nitrogen peroxide with radicals (equation 3 and 4) <sup>which have been assumed in</sup> ~~is confirmed~~ by results of experiments conducted by Schlenk in his study of the reaction of triphenylmethyl with these oxides and other <sup>data</sup> ~~is confirmed~~. We have <sup>insert from bottom of page</sup> succeeded, then, in proving conclusively that ~~the~~ nitroso compounds are the source of <sup>formation</sup> ~~origin~~ of the gem-dinitro derivatives. The <sup>first circumstance from which we proceed in constructing the</sup> ~~primary condition on which we base the formation of~~ <sup>mechanism of formation</sup> ~~gem-dinitro compounds~~ is the extreme ease with which primary and secondary nitroso compounds <sup>are</sup> ~~convert~~ <sup>at</sup> into the corresponding oximes:



The second <sup>circumstance</sup> ~~condition~~ is the extremely rapid interaction between oximes and nitrogen peroxide <sup>dioxide</sup> which leads, in the case of aromatic oximes and <sup>an</sup> ~~excess~~ oxidation, to a <sup>quite</sup> ~~fairly~~ smooth formation of gem-dinitro compounds:



<sup>From</sup> Based on our observations, this reaction takes place with practically <sup>unlimited</sup> ~~limitless~~ speed, even in diluted solutions at <sup>temperatures lower than 0°</sup> ~~0 degree temperature~~. These data, together with previously drawn deductions, prove that the more important stages in the formation of gem-dinitro compounds during nitration

- for example, phenyldinitromethane out of toluene - must be expressed as follows:

$$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{\text{NO}_2} \text{C}_6\text{H}_5\text{CH}_2\text{-NO} \xrightarrow{\text{NO}_2} \text{C}_6\text{H}_5\text{CH(NO)}_2$$

$\rightarrow \text{C}_6\text{H}_5\text{CH=NOH} \xrightarrow{\text{N}_2\text{O}_4} \text{C}_6\text{H}_5\text{CH(NO)}_2$  (formula not legible) (8)

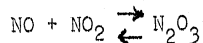
This approach <sup>interpretation of the course of</sup> ~~to the flow of the reaction~~, based on <sup>K</sup> ~~kinetic~~ data, permits us to understand the formation of <sup>the</sup> ~~dinitro~~ compounds and the relationship between the conditions of the nitration process and the yield of mono- and dinitro derivatives (see 1 and 2). For example, the reduction in yield of phenyldinitromethane <sup>with</sup> ~~under~~ an increased concentration of nitrogen peroxide <sup>dioxide</sup> (1) is logically explained by the decreased likelihood of contact between the radical and nitric oxide in favor of its contact with nitrogen <sup>dioxide</sup> ~~peroxide~~  $\text{NO}_2$ ; similarly, a reduced concentration of nitric oxide causes an unbalance of equilibrium ~~(from left to right)~~.

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All the above allows it to be <sup>deduced</sup> ~~concluded~~ with sufficient certainty that the chief primary products of the conversion of alkyls under the conditions of nitration will be a nitroso compound  $\text{R-NO}$ , an alkyl nitrite  $\text{R-ONO}$ , and a nitro compound. We have ... etc

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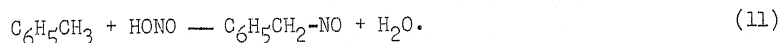
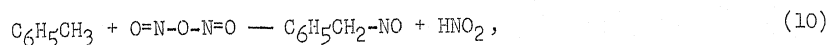
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from left to right. The analogous action of increased temperature (2) conforms to a marked reduction in the solubility of nitric oxide and to a sharp increase in the dissociation of  $\text{N}_2\text{O}_4$  (i.e., an increase in the partial tension and relative  $\text{NO}_2$  content of the solution).

Simple yet fundamental proofs that the mechanism which we proposed for the formation of gem-dinitro compounds was correct were provided us by experiments devoted to a study of the effect of the concentration of the different nitrogen oxides on the overall reaction rate and on the yields of the individual components of the reaction product. The most important result of these experiments is the fact that our theoretical conclusion that the presence of nitric oxide is required for the formation of gem-dinitro compounds was fully substantiated by experiment: the interaction of toluene and nitrogen dioxide in the absence of NO resulted in the output of phenylnitromethane and the other by-products of the reaction with the exception of phenyldinitromethane, which was not formed at all under these conditions. We succeeded in ~~removing~~ eliminating nitric oxide, which is constantly formed from nitrous acid (the latter evolving according to equation (30) and through side reactions, from the sphere of the reaction by reacting nitrogen dioxide with toluene while the mixture was saturated with oxygen.

The fact that the absolute yield of gem-dinitro compounds/~~xxxxxx~~when the concentration of nitric oxide, and consequently/~~xxxxxx~~of  $\text{N}_2\text{O}_3$  and  $\text{HNO}_2$ , is further decreased proves that the active role in the process of formation of gem-dinitro compounds is played by nitrogen dioxide  $\text{NO}_2$  and nitric oxide NO, and not by  $\text{N}_2\text{O}_3$  or  $\text{HNO}_2$ , as could be supposed if it were assumed that -nitrosotoluene ~~xxx~~  $\text{C}_6\text{H}_5\text{CH}_2\text{NO}$  were formed according to the equations:



This result is explained by the decrease in the rate of radical formation, in accordance with equations (3) and (9), as the concentration of nitric oxide decreases.

we take  
If/the results of the interaction of nitrogen dioxide and toluene under as a basis for comparison, ~~then~~ then the normal conditions (with a moderate content of NO) ~~xxxxxxxxxxxx~~

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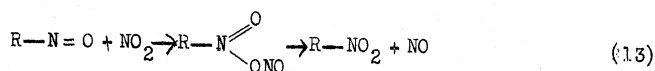
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following characteristics <sup>can</sup> be given ~~for~~ <sup>(1) can increase</sup> for experiments with nitric oxide <sup>content</sup> ~~of a higher concentration~~ and (2) in its absence, by <sup>designating with ± sign</sup> ~~measuring~~ the changes in yield of the reaction product, the nitro compound, and residual oils. For the latter, the <sup>+ sign</sup> ~~sign~~ will denote the absolute value of the yield; the <sup>- sign</sup> ~~sign~~ <sup>and 0 the</sup> ~~sign~~ to the relative value; ~~the~~ <sup>absence</sup> of the product.

	Designation of experiments	
	1(NO)	2(O <sub>2</sub> )
Total yield	-	+
C <sub>6</sub> H <sub>5</sub> CH(NO <sub>2</sub> ) <sub>2</sub>	-	0
	+	0
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NO <sub>2</sub>	-	+
	-	+
Residual oils	-	+
	-	+

It is easy to show that <sup>all these data</sup> ~~the results of this experiment conform to~~ <sup>are in full agreement with</sup> the mechanism <sup>worked out for the reaction</sup> ~~the development of the reaction mechanism~~. The conclusions drawn from our theory on nitration <sup>(concerning)</sup> ~~regarding~~ the possibility of obtaining gem-dinitro compounds <sup>by</sup> ~~through~~ the action of nitric acid on alkylbenzenes were confirmed by the experiment. <sup>Up to</sup> ~~At the~~ present time, our method <sup>has been</sup> ~~is~~ <sup>for</sup> used successfully in the extraction of dinitro derivatives <sup>of</sup> ~~of~~ xylenes, ethylbenzene, diphenylmethane, and tetralin. <sup>The formation of</sup> ~~These~~ lower gem-dinitroparaffins <sup>are formed through nitration</sup> ~~are formed through nitration~~ of ketones with nitric acid <sup>(probably also proceeds through)</sup> ~~a stage in which nitroso compounds are~~ <sup>formed</sup> ~~formed~~ <sup>probably passed through</sup> ~~Worstall's~~ (5) data on the nature of dinitro compounds obtained through nitration of n-~~alkyl~~ paraffins require further definition.

Let us explore briefly other possible ways of converting nitroso compounds under conditions of nitration. In all cases of nitration, <sup>of the conversion</sup> ~~the conversion~~ product of tertiary nitroso compounds is, evidently, the corresponding nitro derivative:



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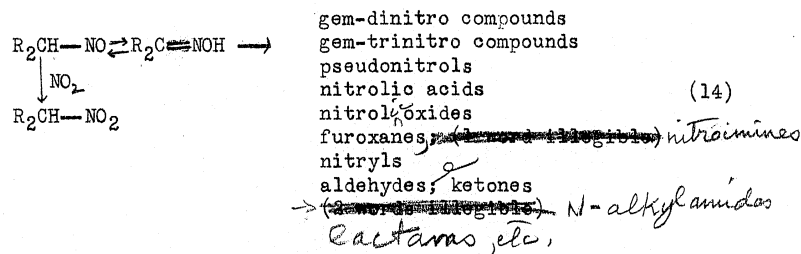
[no. 11] This circumstance explains the fact that the formation of tertiary nitro-paraffins is smoother than that of primary or secondary nitro compounds. It is also possible that ~~the conversion of~~ <sup>are converted</sup> primary and secondary nitro compounds ~~takes place~~ <sup>to a greater or lesser degree</sup> in accordance with the last equation, especially during nitration in the gaseous phase, when conditions for isomerization into oximes, or for ~~change~~ <sup>transformation</sup> into anion ( $R_2C - NO$ )<sup>1</sup>, are unfavorable.

Aliphatic ketoximes, according to Scholl's experiments [6], and aldioximes, <sup>according to</sup> ~~based on~~ our data, produce, respectively, ~~a~~ considerable yields of pseudonitrols and nitrolic acids when ~~applied to~~ <sup>acted on by</sup> nitrogen peroxide at a low temperature, ~~under refrigeration~~. There is reason to believe that under these circum-

stances the formation of small quantities of gem-dinitro compounds takes place. <sup>Under the normal conditions of nitration of paraffins at an increased temp.</sup> ~~(one sentence illegible)~~ <sup>arises the pseudonitrol and nitrolic acids formed as intermediate products must be converted into carbonic acids</sup> Based on available experimental data it can be concluded that ~~It must be concluded from the amount of known experimental data that~~ nitrolic acids can convert into furoxanes, isocyanates, and other products.

either directly, or through the intermediate formation of nitro<sup>ic</sup> oxides  $R - C \equiv N = O$ . The formation of furoxanes <sup>as a result of</sup> during nitration was discovered by Gabriel [7]; the presence of picric acid ~~in~~ <sup>in the product of the</sup> nitration of toluene <sup>[8]</sup> can be explained by the conversion of phenylisocyanate. The possible <sup>i. e. of the</sup> conversion, in the nitration process, of oximes into nitryls, their hydrolysis, and, finally, the Beckman rearrangement, must all be taken into account.

<sup>Upon reflection</sup> ~~In summing up this analysis~~, the most <sup>probable</sup> ~~possible~~ possible conversions of nitro-compounds under conditions of nitration can be expressed as by the following scheme:



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~~Immediately~~ When <sup>there is</sup> ~~exposed to~~ <sup>nitrogen dioxide</sup> ~~nitrogen peroxide~~ <sup>a</sup> sufficiently strong concentration the aromatic nitro compounds - oximes of the benzaldoxime type - <sup>must be</sup> ~~converted~~ <sup>converted</sup> almost completely into gem-dinitro compounds, <sup>which</sup> ~~admittedly~~ makes alkylbenzenes the most suitable subject for the a study of the mechanism of the basic reaction.

## EXPERIMENTAL SECTION

Dioxide

### 1. The <sup>Effect</sup> ~~Influence~~ of the Concentration of Nitrogen Peroxide and Temperature on the Relative Yields of Mono- and Dinitro Derivatives

(a) Equal quantities of nitrogen <sup>dioxide</sup> ~~peroxide~~ (25 <sup>ml</sup> ~~milliliters~~) and anhydrous copper sulfate (20 <sup>g</sup> ~~grams~~) were mixed with <sup>different</sup> ~~various~~ quantities of toluene; the mixtures were placed in conical <sup>flasks</sup> ~~retorts~~ with ground chloro-calcium chloride <sup>calcium chloride</sup> tubes, which had been packed with anhydrous <sup>nitrate</sup> ~~calcium~~ and left to stand <sup>for a period of 30 days at a temperature of approximately 20 degrees</sup>. As <sup>has</sup> ~~been~~ described <sup>above</sup> (9), nitro derivatives were separated after the reaction mass was treated with water.

	Quantity of toluene <sup>in ml</sup> <del>(milliliters)</del>		
	1000	250	50
Yield $C_6H_5CH(NO)_2$	23.5g	7.3g	2.6g
Yield $C_6H_5CH_2NO_2$	5.0g	3.9g	2.1g

(15)

In the first experiment, the solution rapidly acquired a green color <sup>due to</sup> ~~through~~ the formation of  $N_2O_3$ ; in the third <sup>experiment</sup> ~~experiment~~ the solution had an almost brown color, while in the second it <sup>was of</sup> ~~had~~ an intermediate <sup>pink</sup> ~~color~~.

(b) The experiment at 20 <sup>degrees</sup> ~~degrees~~ was conducted under the conditions described above. In the remaining experiments the reaction took place in <sup>flasks</sup> ~~retorts~~ with ground reflux condensers and tubes for the introduction of gaseous nitrogen <sup>dioxide</sup> ~~peroxide~~; at 40 degrees the heating period was 40 hours; at 70 degrees the introduction of nitrogen <sup>dioxide</sup> ~~peroxide~~ took one hour, followed by a two-hour <sup>exposure to</sup> ~~lag~~ 95 degrees; the addition of  $N_2O_4$  took four hours, with <sup>an exposure</sup> ~~an exposure~~ of one hour.

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	Temperature of reaction			
	20°	40°	70°	95°
Yield $C_6H_5CH(NO_2)_2$	23.5g	18.4g	6.8g	1.4g
Yield $C_6H_5CH_2NO_2$	5.0g	7.2g	15.9g	13.4g

(16)

In the third and fourth experiments, the solution had the clear brown color of nitrogen ~~peroxide~~ <sup>dioxide from whole</sup> during the ~~entire~~ time that the reaction took place.

## 2. Chemical Stability of Phenylnitromethane under the action of Nitrogen ~~Peroxide~~ and Nitric Acid

Phenylnitromethane <sup>dioxide was</sup> ~~also proved to be~~ stable with <sup>respect</sup> ~~regard~~ to nitrogen ~~peroxide~~ when heated with acetic acid in a water bath. Exposed to the action of nitric acid under the same conditions, considerable quantities of benzoic acid were formed; however, as in the other experiments, no phenyltinitromethane was obtained.

## 3. Proof of the Necessity for the Presence of Nitric Oxide in the Sphere of Nitration for the Formation of Gem-Dinitro Compounds

Three mixtures were prepared, each of which consisted of 18.4 grams of nitrogen ~~peroxide~~ <sup>dioxide</sup> and 2 ~~liters~~ <sup>liters</sup> of toluene. In the first experiment the reaction was conducted under normal conditions; in the second ~~one~~ the mixture was first saturated with nitric oxide; <sup>in</sup> the third experiment the reaction was conducted under continuous saturation with oxygen fed through a gasometer; in order to assure optimum saturation with oxygen, the flask containing the reaction mixture was periodically agitated.

<sup>no IV</sup> In the first case the solution <sup>gradually</sup> soon began to acquire the green color of  $N_2O_3$ ; in the second case, <sup>of course,</sup> ~~naturally,~~ it had that color from the start, and in the third the solution retained the brown color of  $NO_2$  throughout the experiment.)

<sup>no IV</sup> The initial intensity of the brown coloring <sup>of</sup> during the gaseous phase <sup>in</sup> of the experiments with saturated nitric oxide was markedly weaker than in the remaining cases; this was due to a drop in the partial tension of the monomer of nitrogen ~~peroxide~~ <sup>dioxide</sup>.

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According to  
Based on rough calculation, the concentration of nitric oxide in the reaction mass of this experiment was higher than that of the monomer of nitrogen peroxide.

The mixtures were left at room temperature for six days; after appropriate processing, the following quantities of various products were found in each of these mixtures.

	Order of experiments		
	1	2	3
phenylnitromethane	3.7 g	2.3 g	4.8 g
phenyldinitromethane	14.8 g	11.7 g	--- (17)
benzoic acid	0.1 g	0.1 g	0.1 g
residual oils	10.8 g	8.7 g	29.3 g

WFF (conformance with the requirements)  
In confirmation of our theory, no phenyldinitromethane was produced in the third experiment. Similarly, the proportion of products separated in all experiments proved to be as expected.

Extraction with potassium bicarbonate and soda, in the third experiment, yielded a product of nearly 0.8 grams. The bicarbonate<sup>te</sup> extraction, after a series of <sup>purifications</sup> ~~siftings~~, yielded about 0.1 grams of yellowish needles <sup>(mp 105°)</sup> ~~a substance with a melting point of 105 degrees~~, probably 2,4,6-trinitro-m-cresol. ~~The carbonate extract yielded~~ as well as an insignificant quantity of a crystalline substance which proved to be 2,6-dinitro-p-cresol. In all experiments, the residual oils - as will be pointed out in later <sup>works</sup> ~~studies~~ - consisted mainly of benzyl alcohol and its ethers <sup>[or esters]</sup>.

#### Production 4. Extraction of Phenyldinitromethane through Nitration of Toluene

Below are the details of the experiment which <sup>gave</sup> ~~produced~~ the optimum <sup>best</sup> yield of the desired product.

1.500 <sup>ml</sup> ~~grams~~ of toluene, 10 <sup>g</sup> ~~grams~~ of nitric oxide, and 30 <sup>g</sup> ~~grams~~ of anhydrous copper sulfate were placed in a conical <sup>flask</sup> ~~retort~~ with a ground calcium chloride tube which was packed with anhydrous nitrate of calcium, <sup>with nitric acid at a low temperature</sup> ~~of calcium~~. This mixture was saturated <sup>(to stand)</sup> ~~under refrigeration~~, until it increased in weight by one gram, and was then left at a temperature of 25-30 <sup>°C</sup> ~~degrees~~.

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In the course of the first nine days, ~~an increase of~~ <sup>8</sup> 10 grams of nitrogen dioxide <sup>added</sup> was ~~observed~~ at the end of each three-day interval. At the end of six more days the reaction mass was ~~processed~~ <sup>subjected to treatment</sup>. After ~~a water wash~~ <sup>being washed with water</sup>, the layer of hydrocarbon was vigorously mixed, for ~~approximately~~ <sup>me</sup> four hours, with 200 ~~milliliters~~ <sup>ml</sup> of a 20 ~~percent~~ <sup>%</sup> solution of potassium bicarbonate; ~~the~~ <sup>during</sup> the second and third hour of mixing, a supplementary ~~amount~~ <sup>me</sup> of 50 ~~milliliters~~ <sup>ml</sup> of a 50 ~~percent~~ <sup>%</sup> (solution of) potash was added. <sup>The</sup> Potassium salt of phenyldinitromethane, which had been separated out <sup>in</sup> during this operation, was filtered, <sup>and washed</sup> ~~washed~~ with water, alcohol, and ether; in this manner 25 ~~grams~~ <sup>g</sup> of pure, coarse crystalline product was obtained.

The ~~product~~ <sup>remaining</sup> ~~left~~ in the solution was later separated by adding bromine, in the form of phenyldinitrobromomethane, to the solution. The bromine derivative ~~could~~ <sup>me</sup> be converted into phenyldinitromethane by ~~processing~~ <sup>treating</sup> it with an alcoholic alkali or alkaline solution, in the presence of potassium iodide.

~~The~~ Acidification of the ~~basic solution~~ <sup>of sulfite</sup> mother liquor ~~derived~~ <sup>which was obtained</sup> from the separation of phenyldinitrobromomethane, ~~produced~~ <sup>yielded</sup> pure benzoic acid. In order to ~~eliminate the bromine which is~~ <sup>eliminate the bromine which is</sup> ~~it is recommended that~~ <sup>a bisulfate solution</sup> be added ~~before addition~~ <sup>prior to the introduction</sup> of ~~the~~ acid.

To extract phenyldinitromethane, the reaction mass was mixed for 4 hours with 100 ~~milliliters~~ <sup>ml</sup> of 10 ~~percent~~ <sup>%</sup> alkali, ~~with~~ <sup>me</sup> 20 ~~milliliters~~ <sup>ml</sup> of diethylamine <sup>being</sup> added to speed the extraction (phenylnitromethane was ~~produced~~ <sup>determined</sup> in this experiment in the form of a dibromide derivative, ~~as a~~ <sup>which was produced</sup> ~~the~~ <sup>had been distilled off</sup> ~~result~~ <sup>by</sup> of the addition of bromine). After ~~elimination~~ <sup>the</sup> of excess toluene the remaining (products ~~of the~~ <sup>the</sup> reaction) were separated (residual oils) at a bath temperature of 50 ~~degrees~~ <sup>me</sup> and at 50 ~~millimeter~~ <sup>mm</sup> residual pressure.

As a result of all ~~these experiments~~ <sup>the treatments</sup> and the appropriate ~~calculations~~ <sup>approximate</sup>, the following ~~figures~~ <sup>data</sup> were obtained on the quantities of the ~~various~~ <sup>different</sup> components and the extent to which toluene <sup>the (entering into reaction)</sup> was utilized in their formation:

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	Grams	Percent
Phenylnitromethane	4.6	10.3
Phenyldinitromethane	27.1	46.7
Benzoic acid	4.3	10.6
Residual oils	14.1	32.4

About 70% <sup>oxide</sup> of the nitrogen peroxide participating in the reaction was used up in the formation of phenyldinitromethane; <sup>considering</sup> ~~and considering~~ that nitric oxide was produced as a result of the oxidation and nitration reactions, the total utilization of nitrogen <sup>oxide</sup> ~~peroxide~~ amounted to more than 85% <sup>of</sup> of the theoretically possible.

In order to obtain one gem-dinitro compound the process ~~is limited~~ <sup>can be</sup> limited to treatment with carbonates, and the ~~remainder~~ <sup>residue</sup>, if needed, <sup>can</sup> ~~could~~ be used over again in the reaction. To obtain phenyldinitromethane more rapidly, although with a somewhat lower yield, the temperature can be raised: 2 days are sufficient to complete the reaction at 40° ~~degrees~~, and less than 24 hours ~~are needed~~ <sup>On the</sup> at 50° ~~degrees~~. <sup>See (I)</sup> First Experiments on Obtaining Phenyldinitromethane through Nitration of Toluene with Nitric Acid of 1.42 <sup>(sp g cc) of 1.16</sup> Centimeters ~~Specific Gravity~~. <sup>According to</sup> Judging on the basis of the theory of this reaction, it is ~~entirely~~ <sup>(positively)</sup> probable that even ~~better~~ <sup>higher</sup> yields of gem-dinitro compounds can be obtained.

## CONCLUSIONS

1. Radicals, <sup>formed</sup> ~~emerging~~ during the initial phase of the nitration of paraffins and the side chain of alkylbenzenes, react chiefly with nitric oxide <sup>and the monomer of nitrogen dioxide to yield nitroso compounds, alkyl nitrates, and nitro compounds as primary products.</sup>
2. Gem-dinitro compounds are the end product of the conversion of primary and secondary <sup>α-</sup> nitroso-alkylbenzenes under conditions of nitration.
3. The proposed mechanism of ~~the~~ formation of gem-dinitro compounds is confirmed by a series of new experimental data, most <sup>important</sup> ~~significant~~ of which must be considered the results of the inquiry into the <sup>effect</sup> ~~influence~~ of nitric oxide on the yield of the dinitro product. No gem-dinitro compounds are formed in the absence of nitric oxide.

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4. The paradoxical influence of <sup>the</sup> temperature and of the concentration of the nitrating agent ( $N_2O_4$ ) on the yield of the mono- and dinitro compounds has received <sup>an</sup> adequate theoretical explanation.

5. Other possible conversions of intermediately <sup>formed</sup> ~~formed~~ nitroso compounds in different cases of nitration were examined.

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